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Perturbations in the infra-red bands of SrO

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With 6 figures in the text

Abstract

This paper comprises an extension of the analyses of the infra-red $^1\Sigma - {}^1\Sigma$ band-system of strontium oxide, treated in a previous investigation (ALMKVIST and LAGERQVIST, 1949). Special attention has been paid to perturbations. About 30 perturbations have been found in the upper levels $v' = 0, 1, 2, 3$ and 4. It seems likely that the perturbations are caused by interactions with four different electronic states or sub-states. B-values for some of the perturbing levels have been determined with rather great accuracy. All perturbing states have band-constants of about the same magnitude. By using calculated values for some perturbing matrix elements, it has been possible to estimate the deviations of the upper rotational levels due to perturbations. From these the origins of the bands have been determined rather accurately.

§ 1. Introduction

In the earlier paper we gave the rotational and vibrational analyses of an infra-red $^1\Sigma - {}^1\Sigma$ band-system of SrO. Thus we treated the 4,1, 3,0, 3,1, 2,0, 1,0, 0,0 and 0,1 bands. The analyses of all these bands were made on plates taken in a first order of a Wood's 21 ft concave grating (with a dispersion of 0.95 to 1.15 Å/mm in the region in question). The bands contain strong perturbations, some of them of such a magnitude that they completely destroy the vibrational scheme. The Figures 2 and 4 in the paper already mentioned show the appearance of some of the perturbed levels. We also tried to explain most of the perturbations as being the result of interactions between the upper Σ-state — called Σ^* — and two perturbing electronic states — called P and Q. For this reason we constructed the Figures 3 a and 3 b representing term values of Σ^* and the two states P and Q. The perturbing states were placed in such a way that the lines corresponding to their term values cut the analogous Σ^*-lines just at the perturbations. It is, however, possible to draw these lines in different ways, and for this reason we considered it convenient to investigate the perturbations more thoroughly. In this paper we give our new results. To study the perturbations more closely we were obliged to measure some new parts of the spectrum and also all the weak lines in the

Table 1

Wave-numbers for the 0,0 band.

J	R (J)		P (J)		J	R (J)		P (J)	
30	10 853.98				90		10 662.36		10 555.74
31	52.04				91		56.47		48.46
32	49.96	10 882.36			92		50.39		41.33
33	47.67*	77.89	10 808.36		93		44.07		34.13
34	45.10	73.49	04.92	10 837.43*	94		37.05		26.84
35	42.27	69.08	01.27	31.62*	95	10 648.84	28.69		19.25
36	39.06	64.85	797.39	25.88*	96	37.80	17.93		10.94
37	35.56	60.73	93.25	20.07	97	29.13	04.47	10 521.40	01.31
38	31.62	56.85	88.73	14.43	98	21.83		09.13	489.26
39	27.21	53.18	83.85	09.04	99	15.10		499.18	74.59
40	22.43	49.74	78.55	03.86	100	08.58*		90.65	
41		46.49	72.81	798.83	101	02.15		82.62	
42			66.53	94.03	102	595.76		74.84	
43				89.44	103	89.25		67.18	
44					104	82.66		59.49	
.					105	75.98		51.72	
.					106	69.06		43.91	
.					107	61.97		35.95	
68	753.60		673.42		108	54.51		27.84	
69	47.91	780.10*	67.37		109	46.60		19.51	
70	41.40	71.47	60.93		110	38.04		10.82	
71	33.87	63.48	53.92	686.33	111	28.39		01.65	
72	25.23	56.13	46.08	76.18	112	17.27	561.36	391.84	
73		49.50	37.27	66.90	113	04.30	48.85	80.90	
74		43.47	27.30	58.25	114	489.49	37.33	68.52	12.70
75		38.00		50.39	115		27.84	54.34	99.03
76		32.47		42.98	116		18.65	38.41	86.18
77		27.16		36.04	117		10.09		75.40
78		21.68		29.36	118		01.79		65.03
79		15.47		22.75	119		493.48		55.21
80	13.67			15.99	120		84.55		45.73
81	08.10			08.58	121				36.20
82	02.76		05.43		122				26.12
83	697.27		598.65						
84	91.87		91.98						
85	85.88		85.29						
86	78.55	689.48	78.48						
87		81.13	71.21						
88		74.27	62.66	573.55					
89		68.20		64.00					

background, while the intensity of the so-called companion or extra lines, which are of great importance in the analysis, is very small.

This new investigation leads us to suppose the existence of four perturbing electronic states, here called X, Y, Z and Q. One of these, Z, is identical with that previously called Q. X is probably a $^1\Sigma$-state. All perturbing states have B-values of the magnitude 0.25 and ω-values of the magnitude 450 cm^{-1}. Some X-perturbations give a good idea of the X-state. The Y-state is less well-defined. Z and Q are badly defined, especially Q. The absolute numbering of the vibrational quantum numbers of the perturbing states cannot be established, as the lowest level, $v' = 0$, of Σ^* is also perturbed.

§ 2. Structure of the bands

In this paper we give the wave-numbers of the band-lines hitherto unpublished. To obtain better surveyability we have in some cases also given a few lines already published. The new measurements given in Tables 1—6 show that some wave-numbers already published must be altered a little. In the bands, in which perturbations have been found, two columns for both R and P-lines are given, one for each of the interacting levels. For many perturbations, the two companion lines have been found for several J-values. Overlapped lines are marked with an asterisk.

The 0,0 band. Previously the analysis was followed up to R (79) and P (80). The new analysis extends to R (120) and P (122). We have also found companion lines at some perturbations at lower J-values than $J = 80$. Table 1 contains the new lines. Two lines, namely P (35) and R (79), are altered; the former just a little, the latter more due to an increasing perturbation. Two extra lines, R (19) = 10 866.74 and P (21) = 10 839.06* cm^{-1}, were found but are not given in Table 1.

The 0,1 band. Table 2 contains only the perturbed lines at the perturbation at $J \sim 38$. Five lines, namely R (36), P (37), P (43), R (44) and P (46), are altered a little. The first four appear in Table 2, P (46) is situated at 10 135.62. P (62) is situated at 10 068.38, not at 10 063.38 as previously published (printing error).

Table 2

Wave-numbers for the 0,1 band.

J	R (J)		P (J)		J	R (J)		P (J)	
33	10 204.61		10 165.35		39	10 185.09	10 211.11	10 141.81	10 166.90
34	02.21		61.97		40		07.83	36.60	61.97
35	199.49		58.50		41		04.61	30.97	57.10
36	96.47	10 222.18	54.72		42		01.80		52.53
37	93.12	18.34	50.83	10 177.65	43		199.01		48.14
38	89.35	14.50	46.51	72.16	44		96.23		43.85

Table 3

Wave-numbers for the 1,0 band.

J	R (J)		P (J)		J	R (J)		P (J)	
75	11 341.26		11 251.45		100	11 218.60		11 107.68	11 083.98
76	36.08		45.54		101	10.52		95.19	70.67
77	30.00	11 344.30	39.49		102	04.08		84.90	
78	21.72	34.45	33.06		103	197.11		75.55	
79		27.36	25.73	11 240.00	104	90.33		67.85	
80		21.43	16.13*	28.84	105	83.50		59.64	
81		16.13		20.38	106	76.44		51.63	
82		10.97		13.31	107	68.50		43.51	
83		05.83		06.72	108	56.70	11 168.50	35.19	
84		00.70		00.25	109		59.57	26.01	
85		11 295.51		193.84	110		52.13	12.99	24.83
86		90.28		87.39	111		44.94		14.59
87		84.99		80.91	112		37.71		05.91
88		79.61		74.40	113		30.23		10 997.49
89		74.17		67.84	114		21.84		89.08
90		68.63		61.20	115	22.54	09.85		80.32
91		62.98		54.51	116	12.86			70.65
92		57.28		47.70	117	04.90		10 970.16	57.49
93		51.45		40.80	118	11 097.32		59.26	
94		45.37		33.79	119	89.59		50.07	
95		39.19		26.66	120	82.47		41.24	
96		32.22		19.33	121	74.87		32.20	
97		24.50		11.71	122	67.20		23.98	
98	239.04*	15.20		03.60	123	59.37		15.15	
99	27.64	03.11		11 094.65					

The 1,0 band. The old analysis contained lines up to R (80) and P (80). We have now found lines up to R (123) and P (123). Table 3 gives the result. Extra lines were also found at perturbations at J $\sim$ 47 and J $\sim$ 67. Thus we have detected the lines R (45) = 11 452.32* and P (47) = 11 389.95 cm^{-1} belonging to one of the perturbed levels, and the lines R (46) = 11 439.90, R (47) = 11 434.14, P (48) = 11 376.23 and P (49) = 11 369.17 cm^{-1} belonging to the other.

The 2,0 band. Band-lines were previously given up to R (81) and P (82). In this paper Table 4 gives band-lines up to R (116) and P (118). At the perturbation at J $\sim$ 56 some extra lines were found, namely R (54) = 12 037.59* and P (56) = 11 963.70 belonging to one perturbed level, and R (55) = 12 027.24 and P (57) = 11 951.67 cm^{-1} to the other. We are, however, not completely convinced that these lines are the right ones, but it seems very probable.

The 3,0 band. This band is not represented here by any new lines at higher J-values. We have, however, completed the analysis to lower J-values. The lines detected are given in Table 5.

Table 4

Wave-numbers for the 2,0 and 3,1 bands.

	2,0		3,1	
J	R (J)	P (J)	R (J)	P (J)
80	11 928.86	11 832.94	11 903.79	11 808.32
81	23.62	26.82	898.85	02.33
82	11 919.71	20.60	93.72	796.27
83	14.28	14.05	87.75*	90.10
84	09.08	11 808.87	11 887.75*	83.67
85	03.79	02.33	81.08	76.49
86	898.68	795.66	75.56	11 775.08
87	93.31	89.12	70.22	67.22
88	87.88	82.73	64.96	60.38
89	82.44	76.06	59.62	53.82
90	76.91	69.39	54.28	47.27
91	71.24	62.66	48.85	40.77
92	64.96	55.84	43.41	34.02
93	860.83	48.93	37.89	27.34
94	54.57	41.48	32.31	20.64
95	48.68	736.04	26.69	13.84
96	42.78	28.38	20.93	07.02
97	36.80	21.26	15.11	00.10
98	30.79	14.08	09.23	693.12
99	24.75	06.88	03.18	86.07
100	18.39	699.56	796.97	78.97
101	12.75	92.22	90.39	71.64
102	06.28	84.66	82.98	64.17
103	799.94	677.80	72.73	56.33
104	93.55	70.04	—	47.64
105	87.09	62.46	70.03	36.22
106	80.58	54.84	63.20	
107	74.01	47.09	56.54	631.01
108	67.38	39.33	49.92	22.92
109	60.67	31.51	744.42	15.09
110	53.93	23.66	37.22	07.23
111	47.18	15.73	30.61	600.42
112	40.32	07.75	23.91	576.33
113	33.21	599.68	17.28	68.40
114	26.10	91.52	10.50	60.43
115	18.87	83.31	03.67	52.46
116	11.21	75.02	696.79	44.28
117		66.55		
118		57.66		

Table 5

Wave-numbers for the 3,0 band.

J	R (J)	P (J)
8	12 725.12	
9	24.66	
10	24.12	12 712.31
11	23.48	10.47
12	22.77	08.63
13	22.02	06.59
14		04.62
15		02.49

At the perturbation J ~ 62 some extra lines were discovered: R(60) = 12 632.14, P (62) = 12 550.10*, R (61) = 12 610.68 and P (63) = 12 527.03*.

The 3,1 band. Several new lines at higher J-values have been analysed. They are collected in Table 4. Some extra lines at the perturbation at J ~ 61 were found, namely R (60) = 11 994.97*, P (62) = 11 913.30*, R (61) = 11 973.50 and P (63) = 11 890.51 cm^{-1}. The analysis of the lines at the end of the band is incomplete.

Table 6

Wave-numbers for the 4,1 band.

J	R (J)		P (J)		J	R (J)	P (J)
60	12 588.58		12 517.31		68	12 560.92	12 480.23
61	84.04		12.16		69	56.56	74.51
62	78.82	12 594.54	06.86		70	52.17*	68.85
63	72.04	85.78	01.08		71	47.83	63.22
64	62.65	79.47	494.55	12 510.32*	72	43.35	57.56
65		74.33	86.54	500.20	73		51.92
66		69.71	75.74*	492.63	74		46.11
67		65.27		86.18			

The 4,1 band. The analysis has been extended to higher J-values. The lines are given in Table 6. Extra lines were found at the perturbations at J ~ 29 and J ~ 51, namely R (28) = 12 666.11* and P (30) = 12 626.66*, R (50) = 12 620.97 and P (62) = 12 552.43 cm^{-1}.

§ 3. Perturbations

a. Treatment of the perturbations

In all we found about 30 perturbations in the five upper vibrational levels, v′ = 0 to v′ = 4. Some of the perturbations are very large (see Figures 2 and 4 in our previous paper). From their appearance we can conclude that the B-values of the perturbing states are always less than B′. In several of the perturbations companion lines were found (Tables 1–6).

The perturbations — especially the weaker ones — have been detected by GERÖ's method (1935). For bands with only P and R-branches and in which the perturbations are in the upper state, it is convenient to study the following expression

$$\frac{T}{4\,J} = \frac{R\,(J-2) - R\,(J-1) + P\,(J) - P\,(J+1)}{4\,J} = B'' - B' + 6\,D'' - 2\,J^2\,(D'' - D'). \qquad (1)$$

If the left-hand side of this expression is plotted against J, the points lie on a straight line if $D'' \sim D'$, giving the difference $B'' - B'$. At a perturbation, displacements from the straight line occur. The errors in T/4 J increase, of

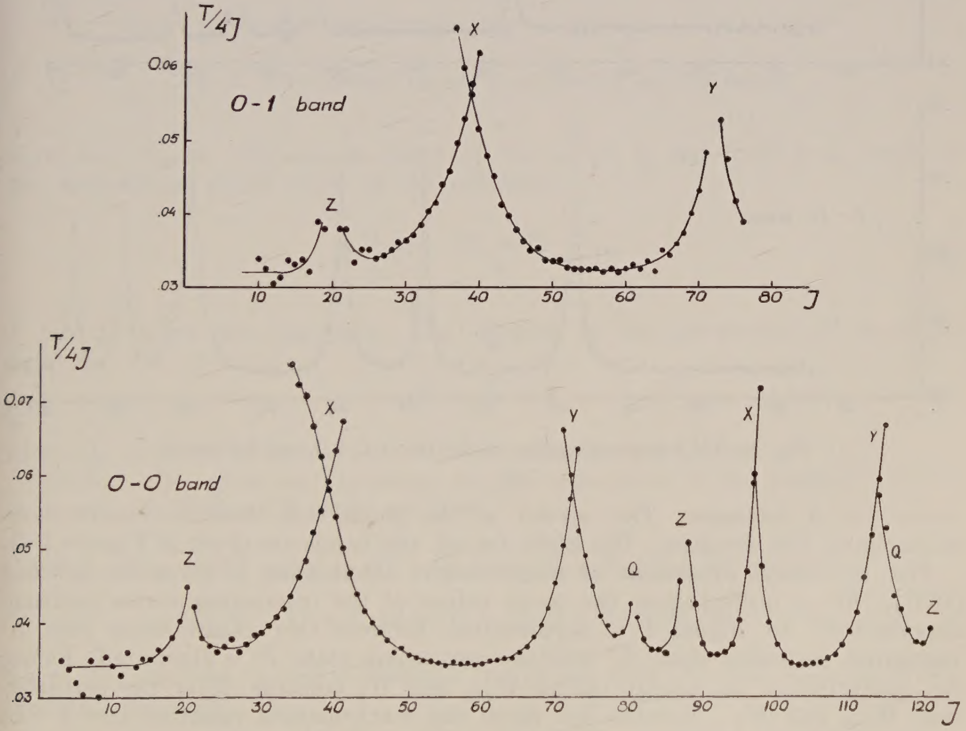

Fig. 1. T/4 J plotted against J for the 0,1 and 0,0 bands.

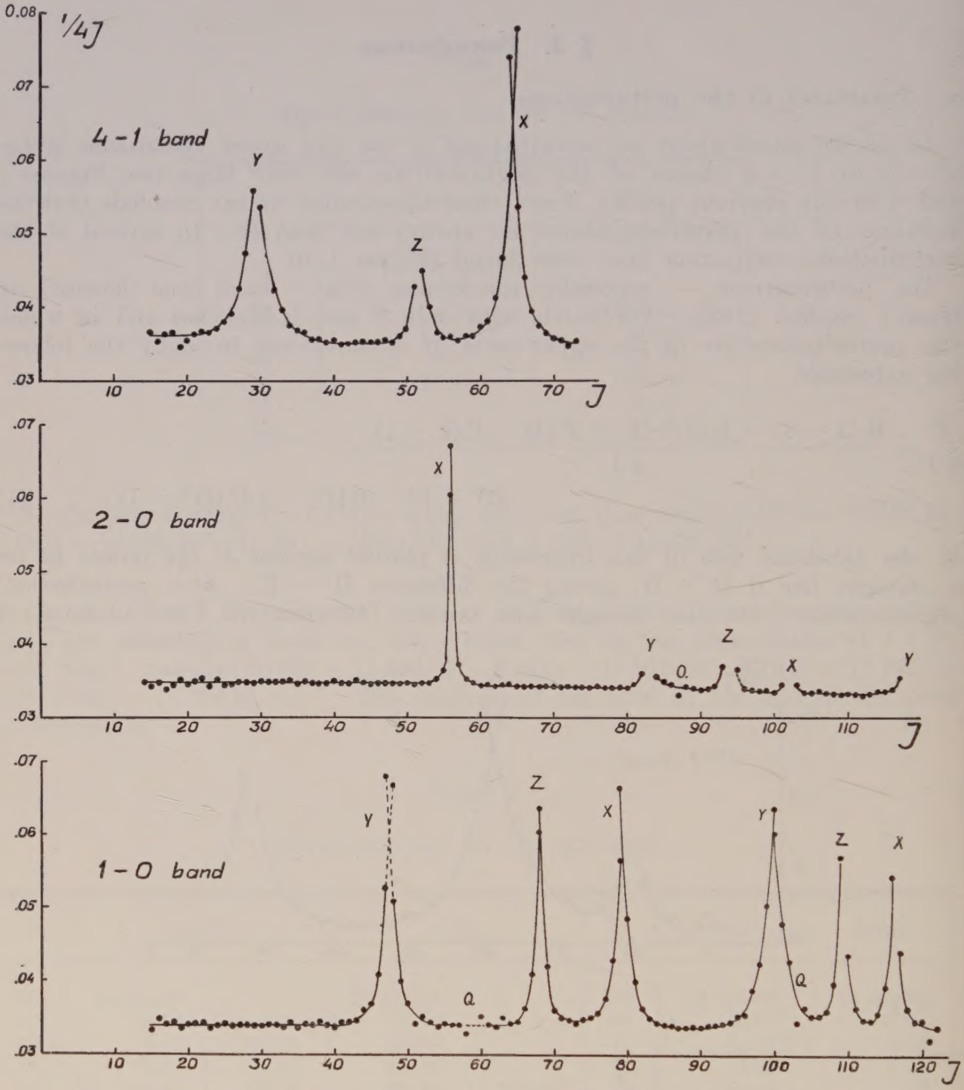

Fig. 2. T/4 J plotted against J for the 4,1, 2,0 and 1,0 bands.

course, as J decreases. The scatter of the points will therefore become considerable at low J-values. The plots for all the bands are given in Figures 1—3.

The theoretical treatment of singlet-singlet interactions is given by KovÁcs (1937). At a perturbation the mean values of the interacting states continue unperturbed. In Figure 4 a perturbation between two singlet states (the investigated perturbed state Σ^* and the perturbing state P) is illustrated. Before the perturbation the energy curves W_{unp} and W_2 coincide, after the perturbation W_{unp} and W_1. KovÁcs has given the mathematical equation (see § 3 b) for the curves f_1 and f_2 (see Figure 5) representing the values of T/4 J in the

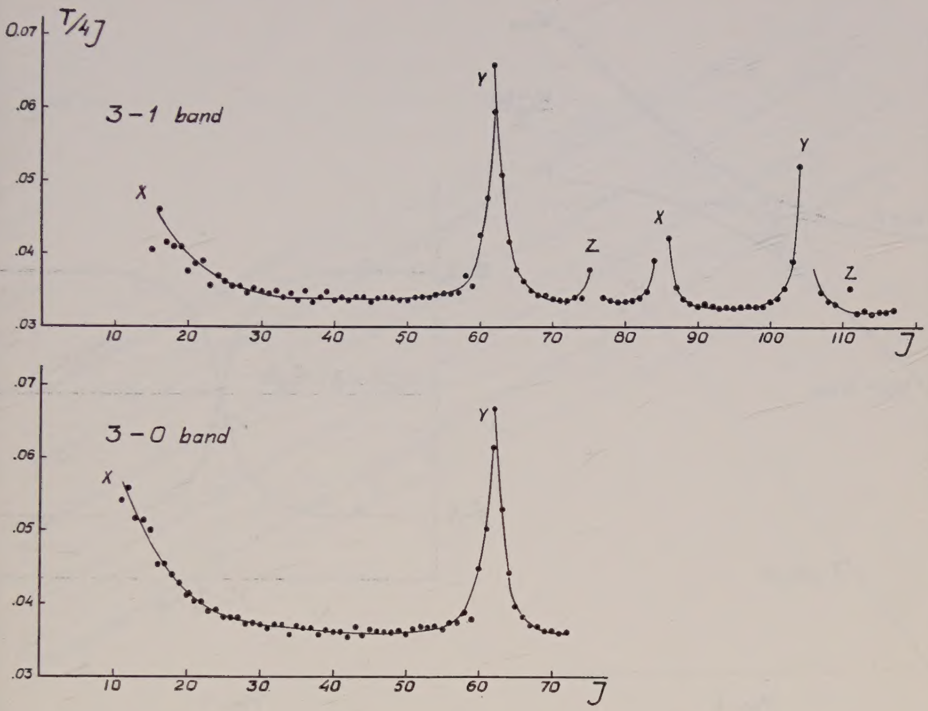

Fig. 3. T/4 J plotted against J for the 3,1 and 3,0 bands.

perturbed region. The mean values of the curves f_1 and f_2 (and of course of the intersection point) occur at the ordinate

$$\frac{f_1 + f_2}{2} = \frac{B_p + B'}{2} - B'' \tag{2}$$

if the D-values are neglected. The J-value at the intersection J^* is almost equal to

$$J^* = J_0 + \tfrac{1}{2} \tag{3}$$

where J_0 is the J-value at which the perturbation culminates.

Kovács also gives an expression for the separation of the levels Σ^* and P at $J = 0$. If P is a $^1\Sigma$ state, we have

$$\begin{aligned} C_{\Sigma\Sigma} = & -2(\nu_0 - B'') + \tfrac{1}{4}\{[P_1(J) + R_1(J-2) + P_2(J) + R_2(J-2)](J+1) - \\ & - [P_1(J+1) + R_1(J-1) + P_2(J+1) + R_2(J-1)](J-1)\}, \end{aligned} \tag{4}$$

where the suffixes 1 and 2 indicate transitions from W_1 and W_2. If P is a $^1\Pi$-state, we have

$$C_{\Pi\Sigma} = C_{\Sigma\Sigma} + B_\Pi \sim C_{\Sigma\Sigma}.$$

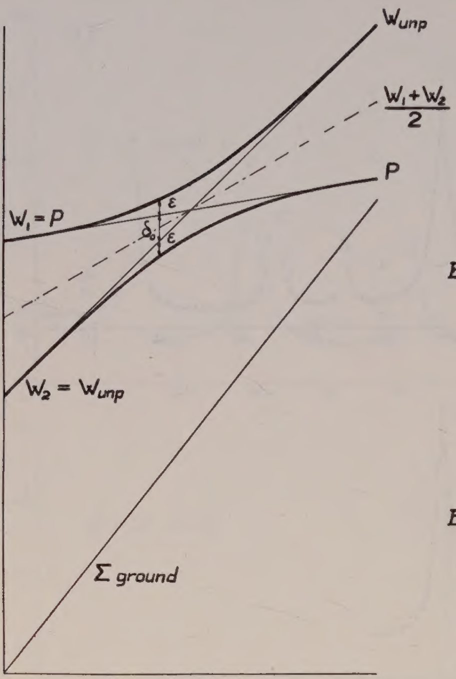

Fig. 4.

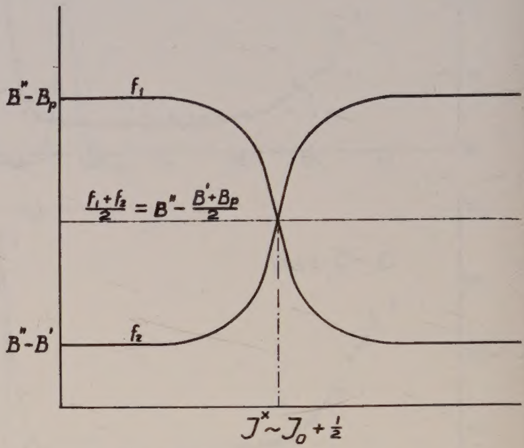
$B''-B_p$
f_1
$\frac{f_1+f_2}{2} = B'' - \frac{B'+B_p}{2}$
$B''-B'$
f_2
$J^* \sim J_0 + \frac{1}{2}$

Fig. 5.

Fig. 4. The course of the energy levels for a singlet-singlet perturbation.

Fig. 5. The variation of T/4 J with J for an interaction between two singlet states.

Another method of obtaining C is to use the energy expressions neglecting the D-values so that we have at once

$$C = \Delta B (J^*)^2 . \tag{5}$$

To distinguish whether the perturbing state P is a $^1\Pi$ or $^1\Sigma$-state we have used the following method. The relation between the magnitude of the deviation ε, the distance δ_0 between the two unperturbed states and the perturbing matrix element H, is

$$\varepsilon (\varepsilon + \delta_0) = |H|^2 . \tag{6}$$

For a $^1\Sigma\,^1\Sigma$ perturbation $|H|^2$ is independent for J, for a $^1\Pi\,^1\Sigma$ interaction it is proportional to $J(J+1)$. ε and δ_0 can be determined in the following way

$$\delta_0 = (B' - B_p) [J(J+1) - J_0 (J+1)].$$

$(2\varepsilon + \delta_0)$ is the differences between W_1 and W_2 at a given J-value, that is $(2\varepsilon + \delta_0)_J = R_1(J-1) - R_2(J-1) = P_1(J+1) - P_2(J+1)$. Thus, if $\varepsilon(\varepsilon + \delta_0)$

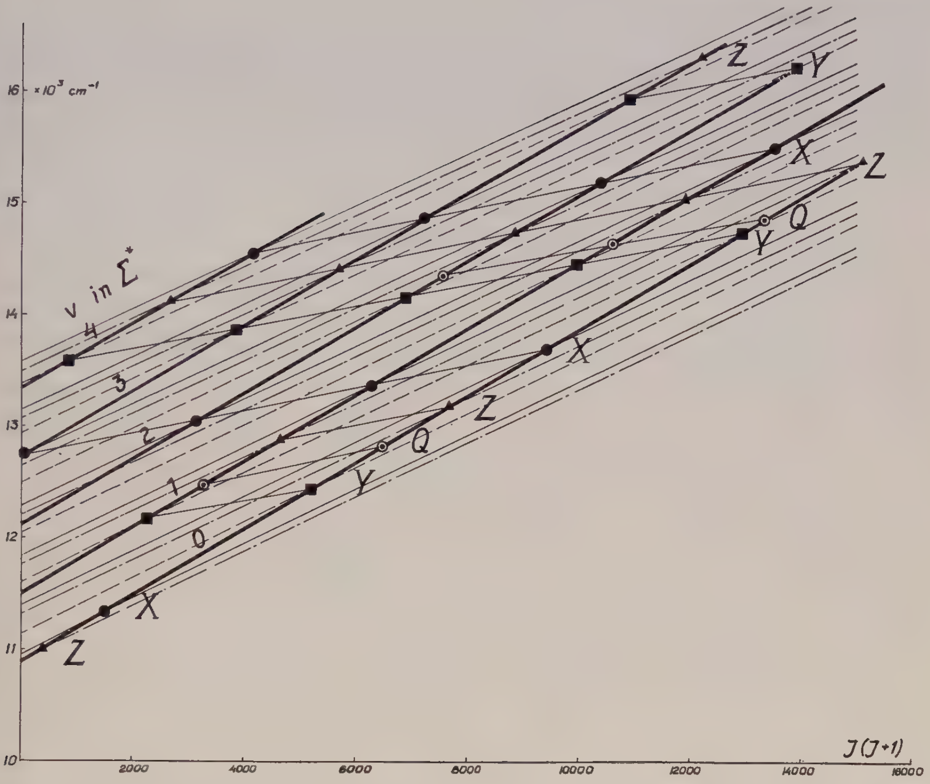

Fig. 6. Perturbations in SrO: term values plotted against J (J + 1). Σ*: thick lines. The perturbing states X, Y, Z and Q: thin lines.

is constant for different J-values, P is a $^1\Sigma$-state, whereas if $\frac{\varepsilon(\varepsilon + \delta_0)}{J(J+1)}$ is constant, P is a $^1\Pi$-state. Another method of detecting $^1\Sigma{}^1\Sigma$ perturbations will be indicated in connection with the X-state (see § 3 b).

The energy levels of Σ* and their perturbations are illustrated in Figure 6, where the rotational energy (B J (J + 1)) is plotted against J (J + 1). The treatment given below shows that the most probable assumption is that which explains the perturbations as the results of interactions with four perturbing states. The energy curves for these states and Σ* are drawn in Figure 6. The four perturbing states are called X, Y, Z and Q. In Fig. 6 interactions with X, Y, Z and Q are marked by solid circles, squares, triangles and circles containing dots, respectively.

In the level v′ = 3 at J ~ 59 an irregularity was detected, which cannot be explained as a perturbation with any of the states X, Y, Z and Q. It is, however, very small and it is not out of the question that the analysis here may be a little uncertain.

b. The X-state

This state is the best well-defined of the four perturbing states. Table 7 shows the data obtained for these perturbations. In Figure 6 they are marked by solid circles. In all 9 perturbations were found.

Table 7

Constants of the X-state.

v′ in Σ*	J*	vp	Bp from Equ. (2)	Bp from Equ. (7)	Bcalc.	C from Equ. (2)	C from Equ. (5)	C mean (weighted)
0	38.9	x + 0	0.2513 (12)		0.2513	10 949.$_7$	10 948.$_8$	10 949.$_5$
0	97.1	x + 1	0.250$_4$ (2)		0.2493	11 388.$_5$	11 387.$_5$	11 388.$_4$
1	79.3	x + 2	0.247$_7$ (1)		0.2473	11 840.$_2$	11 837.$_7$	11 839.$_0$
1	116.3	x + 3		0.244	0.2453		12 267.$_2$	12 284.$_0$
2	56.1	x + 3	0.244 (1)			12 286.$_7$	12 282.$_4$	
2	~ 102.0	x + 4		0.243	0.2433		12 715.$_4$	12 719.$_7$
3	~ 8.0	x + 4					12 720.$_2$	
3	~ 85.0	x + 5			0.2412		13 146.$_2$	13 146.$_2$
4	64.4	x + 6	0.238$_6$ (2)		0.2393	13 587.$_7$	13 576.$_1$	13 584.$_6$

It is of great interest to investigate whether the perturbing X-state is a $^1\Sigma$ or $^1\Pi$-state. This we have done in the way mentioned above. Thus the product $\varepsilon(\varepsilon + \delta_0) = |H|^2$ is formed. Table 8 gives the result for the perturbation at $J^* = 38.9$ in the 0,0 band. The table shows very clearly that the product $\varepsilon(\varepsilon + \delta_0)$ is independent of J, indicating that the X-state is a $^1\Sigma$-state. The third column in Table 7 gives the vibrational quantum number. As we cannot decide the absolute numbering, the lowest level is given as x, the next as (x + 1) etc. The fourth column in the same table contains the B-values, B_p or B_x, of the perturbing state determined by the method described above (Equ. (2)). The number of determinations of a certain B_p-value at a perturba-

Table 8

J	$\lvert H\rvert^2 = \varepsilon(\varepsilon + \delta_0)$	$\lvert H\rvert^2/J(J+1)$
33	155.7	0.1388
34	155.8	0.1309
35	157.2	0.1248
36	157.1	0.1119
37	157.7	0.1122
38	157.8	0.1065
39	158.1	0.1013
40	157.6	0.0961
41	156.8	0.0911
	mean 157.1	

tion is given in brackets. From this we see that the perturbation at $J \sim 39$ in $v' = 0$ gives the most information about the perturbing state. This is also apparent from Fig. 1. This perturbation has a lot of extra lines. The accuracy in the B_{x+0}-value 0.2513 is of the magnitude $\pm$ 0.0003. For the B_x-values obtained from only a single determination the error may be estimated at about $\pm$ 0.0015. If a perturbing vibrational level cuts two consecutive vibrational levels of Σ^*, it is also possible to determine the B_p-value from the points of intersection. We have

$$B_p = \frac{B'_{v+1}\,(J^*_{v+1})^2 - B'_v\,(J^*_v)^2 - \Delta G_{v+1,\,v}}{(J^*_{v+1})^2 - (J^*_v)^2}. \tag{7}$$

In this way we can get a value for B_{x+3} from intersections in the levels $v' = 1$ and $v' = 2$.

$$B_{x+3} = \frac{0.3029 \times 116.3^2 - 0.3021 \times 56.1^2 - 615.5}{116.3^2 - 56.1^2} = 0.2438.$$

This value agrees very well with that obtained by the other method. A lot of factors, however, contribute small errors. Such contributions emanate from the error in the determination of the J^*-values, the neglecting of the D-values, the errors in the B'-values and in $\Delta G_{v+1,\,v}$. It seems likely that the resulting error does not exceed $\pm$ 0.002 cm^{-1}. Taking into consideration all the B-values determined (weighted by their errors), the following equation is obtained.

$$B_{x+v} = 0.2513 - 0.0020\,v.$$

Table 7 shows a perturbation at $J_0 \sim 7.5$ in $v' = 3$, though Fig. 2 only gives one of the curves f_1 and f_2. It is nevertheless possible to determine J_0 from the fact that the perturbing matrix element is independent of J. Kovács (loc. cit.) has shown the expressions for the energies W_1 and W_2 and for the curves f_1 and f_2 to be:

$$\left|\begin{array}{lcl} W_1 & = & \frac{1}{2}\,[C + (B' + B_p)\;J\,(J+1)] + U\,(J) \\ W_2 & = & \frac{1}{2}\,[C + (B' + B_p)\;J\,(J+1)] - U\,(J) \\ U\,(J) & = & \sqrt{\frac{1}{4}\,[C + (B' - B_p)\;J\,(J+1)] + |\,H\,|^2} \end{array}\right.$$

$$\left|\begin{array}{lcl} f_1\,(J) & = & \dfrac{B' + B_p}{2} - B'' + \dfrac{U\,(J-1) - U\,(J)}{2\,J} \\ f_2\,(J) & = & \dfrac{B' + B_p}{2} - B'' - \dfrac{U\,(J-1) - U\,(J)}{2\,J} \end{array}\right.$$

From the lowest three equations we can solve $|\,H\,|^2$. We obtain

$$|\,H\,|^2 = \frac{(B_p - B')^2 - (\Delta f)^2}{(\Delta f)^2}\left[\left(\frac{C}{2} + \frac{B_p - B'}{2}\,J^2\right)^2 - \left(\frac{\Delta f}{2}\right)^2 J^2\right]$$

where $\Delta f = f_1 - f_2$.

If Δf is known for two different J-values and B_p and B' also are known, it is possible to obtain C from the right-hand side of this equation ($|H|^2$ is constant). Now we know f_1 for several J-values of the 3,0 and 3,1 bands (see Fig. 3), B' is 0.3008 and Table 7 gives B_p as 0.2433. We can then determine f_2 from Equ. (2) and of course also $(f_1 - f_2)$.

Such calculations have been made for the 3,0 and 3,1 bands. For the 3,0 band at $J = 17$ and 26 we have $f_1 = -0.0448$ and -0.0379. The equation for C gives two solutions with $C_1 = 3.55$ and $C_2 = 22.47$. A similar equation for the 3,1 band (the J-values 18 and 26 were chosen) gives $C_1 = 3.88$ and $C_2 = 24.46$. The average values are 3.7 and 23.5. It is now simple to calculate where the perturbation culminates. We have (Equ. (5))

$$(J_0 + \tfrac{1}{2})^2 (B' - B_p) = C.$$

The two C-values give $J_0 = 7.5$ or $J_0 \sim 45$. The latter is of course impossible (see Fig. 3). The result of the calculation is therefore

$$\begin{cases} J_0 = J^* - \tfrac{1}{2} = 7.5 \\ |H|^2 \sim 45 \\ C = 3.7 \end{cases}$$

The C-values for the different perturbations are calculated by the two methods described above (equations (4) and (5)). All the values are given in Table 7 (here added to $\nu_0^{\Sigma *}$). For some perturbations the agreement is rather poor. This is due especially to the fact that the errors increase with increasing J-values. In the last column we have given weighted mean values. The ΔG-differences show a somewhat irregular course. They are, in order, 438.9, 450.6, 445.0, 435.7, 426.7 and 438.2. They may be given roughly by

$$\Delta G = 442.5 - 3.8\,v.$$

c. The Y-state

Another set of perturbations — in total 9 — is marked by squares in Figure 6. These perturbations must be due to another perturbing state, called Y. Table 9 gives the data obtained for these interactions. The number of extra lines at these perturbations is everywhere rather small. The greatest number of such lines was found at the perturbation $J \sim 72$ in $v' = 0$.

A study of the matrix element of this perturbation gives, however, no definite information on the perturbing state. For $J = 70$, 71, 72 and 73 the product $\varepsilon(\varepsilon + \delta_0)$ has the following values, respectively, 224.6, 220.6, 217.7 and 213.7. This result does not agree so good with the supposition that the Y state is a $^1\Sigma$-state, and makes it impossible that Y is a $^1\Pi$-state. As we have only four values it seems likely to us, however, that Y is a $^1\Sigma$-state. The values are all in the neighbourhood of 220.

The B-values follow approximately the formula

$$B_{v+y} = 0.2529 - 0.0023\,v.$$

Table 9

Constants of the Y-state.

v' in Σ^*	J^*	v_p	B_p from Equ. (2)	B_p from Equ. (7)	$B_{calc.}$	C from Equ. (4)	C from Equ. (5)	C mean
0	72.3	$y + 0$	0.252_9 (3)		0.2529	$11\,146._8$	$11\,138._6$	11 143
0	113.9	$y + 1$	0.252_4 (1)	0.247	0.2506	$11\,566._1$	$11\,565._8$	11 599
1	47.5	$y + 1$	0.251_3 (1)			$11\,592._5$	$11\,606._1$	
1	99.9	$y + 2$	0.247 (1)		0.2483	$12\,033._0$	$12\,054._7$	12 044
2	83.0	$y + 3$			0.2460		$12\,490._1$	12 490
2	~ 118	$y + 4$		0.242	0.2437		$12\,916._8$	12 940
3	62.3	$y + 4$	0.244 (1)			$12\,942._1$	$12\,938._1$	
3	~ 104.5	$y + 5$		0.240_5	0.2414		$13\,365._2$	13 376
4	29.4	$y + 5$					$13\,376._3$	

The weighted means of the C-values give the following Δ G-differences: 456, 445, 446, 450 and 436. They can roughly be given by

$$\Delta G_y = 450 - 1.8\,v.$$

d. The Z-state

A third group of perturbations emanate from interactions of Σ^* with another state called Z (in Figure 6 marked by triangles). The data on the perturbations are collected in Table 10. These perturbations are not so strong as those arising from the X and Y-states. Thus a perturbation that must lie at the beginning of $v' = 2$ is not observed owing to its small matrix element. No determination of the B_z-values from companion lines can be made because such lines are not found to the necessary degree. Two B-values can, however, be calculated from intersections between the vibrational levels of the Σ^* and Z-states. They are $B_{z+2} = 0.244_4$ and $B_{z+6} = 0.237_5$. These values give an α-value = 0.0017. The C-values in Table 10 are calculated from these B and α-values. The Δ G differences are 424, 443, 447, 437, 424 and 424. They vary very irregularly. This is due, of course, to the very bad data obtained for the B-values.

Table 10

v'	J^*	v_p	B_p from Equ. (7)	C from Equ. (5)
0	20.0	$z + 0$		10 893
0	87.6	$z + 1$		11 317
0	~ 122	$z + 2$	0.24_{44}	
1	68.1	$z + 2$		11 760
1	~ 109.2	$z + 3$		12 207
2	94.0	$z + 4$		12 644
3	~ 75.5	$z + 5$		13 068
3	~ 110.5	$z + 6$	0.23_{75}	13 492
4	51.7	$z + 6$		

e. The Q-state

It is possible to detect a further five perturbations which seem to originate from interactions with a fourth state, called Q. Their positions are given in Table 11. In Fig. 6 they are marked by open circles containing dots. They are extremely small. The largest is that situated at $J^* = 80.5$ in $v' = 0$. Some of the other perturbations are difficult to trace in Fig. 1–3, and we have therefore marked their positions in the figures. The only information we can obtain on the B-values is from the points of intersection at $J^* = 59$ in $v' = 1$ and $J^* = 115.5$ in $v' = 0$. This B-value is 0.242. Because of the poor data on the B-values it is scarcely worth while to put $\alpha = 0.002$ and calculate the other B-values and the C-values. They seem, however, to be of the same magnitude in this level as in the others. Only one C-value can be given with any degree of accuracy, namely that from the level passing through $J = 59$ in $v' = 1$. This is 11 700 (added to $\nu_0^{\Sigma *}$).

Table 11

v′	J*
0	80.5
0	115.5
1	~ 59
1	~ 103
2	~ 87

f. Interpretation of the perturbing states

It is very probable that all the perturbing states X, Y, Z and Q are singlets. X behaves exactly like a $^1\Sigma$-state. Y may also be a $^1\Sigma$-state. On the other hand, we have no data on the perturbing matrix elements of the states Z and Q. This fact makes it very difficult to come to any conclusion regarding the states. It is, however, also possible that SrO has triplet states and this raises the question whether the perturbing states, or some of them, may not be triplet sub-states. The resemblance of the B- and ω-values of X, Y, Z and Q may argue in favour of this suggestion. Thus for a $^3\Pi\,^1\Sigma$ interaction — in Hund's case *a* — the perturbing matrix elements are of the form

$$H(^3\Pi_2\,^1\Sigma) = 0, \quad H(^3\Pi_1\,^1\Sigma) = \eta\sqrt{J(J+1)}, \quad H(^3\Pi_0\,^1\Sigma) = 2\,\xi,$$

where ξ and η are constants. The interaction $^3\Pi_2\,^1\Sigma$ does not give any perturbations (unless at high J-values where the case *a* does not hold), the interaction $^3\Pi_1\,^1\Sigma$ gives perturbations of the same appearance as $^1\Pi\,^1\Sigma$ and the interaction $^3\Pi_0\,^1\Sigma$ gives, finally, perturbations of the same type as $^1\Sigma\,^1\Sigma$. It is of course also possible to conceive $^3\Sigma\,^1\Sigma$ interactions. $^3\Sigma^+\,^1\Sigma^+$ interactions give one set of perturbations, $^3\Sigma^-\,^1\Sigma^+$ interactions two. The matrix elements are in both cases J-dependent. Perturbations between Σ-states of different multiplicity is treated by Budó and Kovács (1938–1939). A discussion of

$^3\Pi\,^1\Sigma$ perturbations is given by BARROW, LAGERQVIST and LIND when treating the spectrum of the sister-molecule BaO. A more detailed discussion of the expressions at $^3\Pi\,^1\Sigma$ and $^3\Sigma\,^1\Sigma$ perturbations will be published later on by KOVÁCS and one of us (A. L.).

§ 4. Band origins and vibrational levels in $\Sigma^* - \Sigma$

Using the perturbing matrix elements for the $X\,\Sigma^*$ perturbations at $J = 39$ in $v' = 0$ and at $J = 8$ in $v' = 3$, it is possible to calculate rather accurate origins for bands with the levels $v' = 0$ and 3 as upper levels.

The origin of the 0,0 band was previously determined as 10 868.42 (in our previous paper the origin was owing to a printer's error given incorrectly as 10 868.82). It is now possible to determine the effect of the displacement ε at $J = 0$ from the equation

$$\varepsilon(\varepsilon + \delta_0) = 157.1.$$

We get $\varepsilon_{J=0} = 1.91\ \mathrm{cm}^{-1}$. As the curve $R(J-1) + P(J) \simeq 2\nu_0 + 2(B' - B'')J^2$ shows a weak curvature at lower J-values it is necessary to add a further $0.07\ \mathrm{cm}^{-1}$. The new origin is $10\,870.42\ \mathrm{cm}^{-1}$. For the 0,1 band similar calculations give 10 224.92.

Table 12

J	ε
15	3.35
16	3.01
17	2.72
18	2.45
19	2.22
20	2.01
21	1.82

In a somewhat similar way we can determine the origins of the 3,0 and 3,1 bands. From the equations $\varepsilon(\varepsilon + \delta_0) = 45$ and $\delta_0 = \Delta B\,[(J + \frac{1}{2})^2 - 64]$ the displacements for $J = 15, 16, 17, \ldots, 21$ have been calculated (see Table 12). These corrections have been added to the bandlines $R(J)$ and $P(J)$ and the origins determined in the usual way from the equation

$$R(J-1) + P(J) \simeq 2\nu_0 + 2\,\Delta B\,J^2.$$

We get

$$\nu^0_{3,0} = 12\,716.28$$

$$\nu^0_{3,1} = 12\,070.68.$$

The rotational displacements of the 4,1 band are not so large, and because of this we have determined the origin directly in the usual way. Table 13 gives the origins for all the bands.

Table 13

Origins of the $\Sigma^* - \Sigma$ bands.

v′ ↑ / v″ →	0		1
4			12 680.40
			609.72
3	12 716.28	645.60	12 070.68
	612.68		
2	12 103.60		
	615.47		
1	11 488.13		
	617.13		
0	10 870.40	645.48	10 224.92

The $\Delta G_{v+1,v}$ differences of the upper Σ^* levels now vary rather regularly. A three-constant formula can be determined as follows

$$G'(v) = 619.5_8 (v' + \tfrac{1}{2}) - 0.8_9 (v' + \tfrac{1}{2})^2 - 0.05_4 (v + \tfrac{1}{2})^3.$$

The vibrational constants $\omega_e'' = 653.4_9$ and $x_e'' \omega_e'' = 4.0_0$ for the lower Σ are determined from the band-heads, and for this reason they may be a little unreliable. It is, however, possible to calculate a good value for the difference $G''(1) - G''(0) = \omega_e'' - 2 x_e'' \omega_e''$. For the 0,0 and 0,1 bands we have

$$[R(J-1) + P(J)]_{0,0} = 2 \nu^0_{0,0} + 2 (B_0' - B_0'') J^2$$

$$[R(J-1) + P(J)]_{0,1} = 2 \nu^0_{0,1} + 2 (B_0' - B_1'') J^2.$$

The difference between the equations — called A — is

$$A = 2 (\nu^0_{0,0} - \nu^0_{0,1}) + 2 (B_1'' - B_0'') J^2 = 2 [G''(1) - G''(0)] + 2 (B_1'' - B_0'') J^2.$$

From the 0,0 and 0,1 bands we obtain $(\omega_e'' - 2 x_e'' \omega_e'') = 645.56$, from the 3,0 and 3,1 bands 645.62. The mean is 645.59. The values calculated from the band-heads give 645.49. The agreement is good.

§ 5. Band-constants of SrO

In Table 14 we have collected the band-constants of the electronic states Σ^*, Σ, X, Y, Z and Q. As we do not know the absolute vibrational quantum

Table 14

Band-constants of the known states in SrO.

Electronic state	T_0 in cm^{-1}	ω	$x_e \omega_e$	B_e	α	D_e
Q	$T_q \sim 11\,260$	444		$B_q = 0.242$	0.002	
Y	$T_y \sim 11\,143$	450		$B_y = 0.252_9$	0.002_3	
X	$T_x \sim 10\,950$	443		$B_x = 0.2513$	0.002_0	
Z	$T_z \sim 10\,893$	444		$B_z = 0.248$	0.001_7	
$^1\Sigma^*$	10 870.40	$\omega_e = 619.6$	~ 0.9	0.3047_1	0.0011_2	$0.32 \cdot 10^{-6}$
$^1\Sigma$	0	$\omega_e = 653.4_9$	4.0_0	0.3377_9	0.0020_4	$0.34 \cdot 10^{-6}$

numbers of the perturbing states, the T and B-values are given suffixes indicating the unknown quantum numbers. The values given for the perturbing states are all determined as if the states are all singlets.

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